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Determination of Tungsten and Associated Elements in Natural Brines and Related Process Solutions by Inductively Coupled Plasma Spectrometry

By M. M. Jones and A. B. Whitehead

UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

g	gram	mL/min	milliliter per minute
g/L	gram per liter	mm	millimeter
L	liter	nm	nanometer
L/min	liter per minute	pct	percent
lb	pound	s	second
mg/L	milligram per liter	V	volt
mL	milliliter	W	watt

DETERMINATION OF TUNGSTEN AND ASSOCIATED ELEMENTS IN NATURAL BRINES AND RELATED PROCESS SOLUTIONS BY INDUCTIVELY COUPLED PLASMA SPECTROMETRY

By M. M. Jones[1] and A. B. Whitehead[2]

ABSTRACT

Natural brines are potential domestic resources of minerals. The brines of Searles Lake, CA, for example, contain an estimated one-fourth of our current reserve of tungsten. A key to Bureau of Mines research to recover this critical mineral is the ability to quantitatively measure concentrations of particular constituents in the large number of brine samples and process solutions produced under a multiplicity of test conditions. This paper describes procedures used to determine arsenic, boron, phosphorus, silicon, and tungsten in these solutions by simultaneous inductively coupled plasma spectrometry. A variable internal standard method was used to compensate for tungsten interference on the other analytes in tungsten concentrates, and matching standards were used to determine tungsten in raw brine. Other solutions were analyzed using normal techniques. Analytes were determined down to 1 mg/L with an average precision of 2.5 pct relative standard deviation. Accuracy, estimated using synthetic solutions and by comparison with values obtained by other methods, averaged about 2.5 pct. The methods were rapid, required little sample preparation, and provided the needed sensitivity.

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INTRODUCTION

Research being conducted by the Bureau of Mines to develop the basic technology to recover minerals from domestic resources includes research for the recovery of tungsten from the subterranean brines of Searles Lake, CA. Brine may contain as much as 80 mg/L WO_3 with a total dissolved-salt content of about 450 g/L. In the Bureau's tungsten recovery process (1-2), the feed brine is passed through a column of chelating resin,[3] which removes tungsten and some arsenic, boron, phosphorus and silicon. Sulfide and organic material present in the brine are also found on the resin, but most of the salts and other elements remain in the effluent. The tungsten and concomitants are then eluted from the resin with a 5-g/L-Na_2CO_3 solution. This primary eluate contains up to 1 g/L WO_3. The tungsten is further concentrated in a second chelating cycle, with the secondary eluate containing up to 100 g/L WO_3. Each process stream is sampled frequently during a run, and about 20 of these samples are submitted for analysis.

This research generated a large number of samples to be analyzed for tungsten, arsenic, boron, phosphorus, and silicon. The analyses were performed individually by wet chemical, colorimetric, and atomic absorption methods. Separate sample preparation was required for each element. Tungsten and boron required solvent extraction separation from the matrix prior to determination. The phosphorus determination was very time consuming. It also lacked sensitivity, as did the methods for boron and silicon. Analysis of such samples by simultaneous inductively coupled plasma (ICP) spectrometry offered the advantages of speed, precision, and low limits of detection. Preliminary tests indicated that all required analyses were feasible, and development of optimized procedures was undertaken.

Problems encountered in the development of an ICP method were related to the extremely high salt content of the brine, the spectral interference of tungsten on the other analytes, and the low concentration of tungsten relative to the total salt content. These problems appeared in varying degrees in the different process solutions and were therefore related to a specific sample type. The major sample types requiring analysis were the original brine (feed), the resin column effluent (spent feed), and the primary and secondary tungsten concentrates (eluates). Table 1 shows a summary of sample types and their approximate compositions.

TABLE 1. - Sample types and composition

	Concentration range, g/L		
	Feed	Spent feed	Eluate
Analyte:			
As....	0.2	NAp	0.001- 1.5
B_4O_7..	10	NAp	.001- 1.5
P_2O_5..	.6	NAp	.001- 1.5
Si....	.02	NAp	.001- .3
WO_3...	.08	<0.001- 0.08	.01 -100
Matrix[1].	453	453	1 -450

NAp Not applicable.

[1]Feed breakdown, g/L: 222 NaCl, 99 Na_2SO_4, 56 KCl, 55 Na_2CO_3, 16 $Na_2B_4O_7$, 3 Na_2S, 1 $NaLi_2PO_4$, 1 Na_3PO_4.

In analysis of the feed, the low concentration of tungsten relative to the high salt matrix presented a problem in the determination of tungsten. While the other analytes were readily determined on a diluted sample, in which case the salt content had no significant effect on the analysis, the tungsten determination was less precise than desired. The problem of analyzing the spent feed for tungsten was identical.

The composition of eluate samples varied widely. As elution progressed, tungsten concentration increased while concentration of other analytes decreased. Salt content dropped rapidly to insignificant levels. The first few samples in the elution series, because of high salt concentration, were analyzed in the same way as feed brine. As tungsten values increased, the analytical problem became that of the spectral interference of

[3]QRF resin, developed by the Bureau of Mines.

tungsten on the other analytes. For samples with tungsten concentration up to 1 g/L, programmed interference corrections provided a satisfactory solution to this type of interference. At higher tungsten concentrations, variation in the value of correction factors contributed a significant error in the determination of arsenic, boron, phosphorus, and silicon. For accuracy, it was necessary to redetermine the correction factors with each set of samples. To eliminate this interference, an internal standard method was studied in which tungsten served as a variable internal standard for the other four analytes and was simultaneously determined with them.

INSTRUMENTATION

A Jarrell-Ash Model 975 AtomComp spectrometer[4] equipped with 28 fixed channels, plus a variable wavelength channel, was used in this investigation. Solution was introduced into the plasma with a cross-flow nebulizer assisted by a peristaltic pump. Sample uptake rate was 1.2 mL/min. Operating parameters and analytical wavelengths are given in table 2.

REAGENTS AND STANDARDS

Reagents were prepared with distilled-deionized or double-deionized water and analyzed reagent-grade chemicals.

Standards were prepared from high-purity compounds or from commercially available single-element solution standards. Tungstic oxide (WO_3) was dissolved in 2-pct NaOH, and H_3BO_3 and $NH_4H_2PO_4$ were dissolved in water. Commercial standards were used for arsenic and silicon, each in 2-pct KOH. For each analyte, a single-element, 1-g/L standard was prepared from which diluted mixed standards were prepared. All solutions were prepared and stored in plastic labware.

REAGENTS

Diluent: NaOH, pH 8. NaOH pellets were added to 2 L of water to a pH of approximately 8, as indicated by pH paper.

Synthetic brine, 50 pct: The following chemicals were weighed into a 1,500-mL beaker, dissolved, and diluted to 1 L: 111 g NaCl, 50 g Na_2SO_4, 28 g KCl, and 28 g Na_2CO_3.

STANDARDS AND BLANKS

Direct method:	
Blank.....	NaOH, pH 8.
Standard 1.....	10 mg/L each of As, P_2O_5, and Si; 100 mg/L B_4O_7.
Standard 2.....	10 mg/L WO_3 in pH 8 NaOH.
Matched method:	
Blank.....	1:19 synthetic brine prepared by diluting the 50-pct synthetic brine solution 1:9 with double-deionized water.
Standard 1.....	10 mg/L WO_3 in 1:19 synthetic brine.
Standard 2.....	10 mg/L each of As and Si, 50 mg/L P_2O_5, and 500 mg/L B_4O_7 in 1:19 synthetic brine.
Internal standard method:	
Blank 1.....	NaOH, pH 8.
Blank 2.....	1,000 mg/L WO_3 in pH 8 NaOH.
Standard.....	10 mg/L each of As, B_4O_7, P_2O_5, and Si, and 1,000 mg/L WO_3.

[4]Reference to specific products does not imply endorsement by the Bureau of Mines.

TABLE 2. - Instrumental parameters and analytical wavelengths

Power, W:	
Incident	1,100
Reflected	10
Gas flow, L/min:	
Coolant	19
Auxiliary	0
Sample	0.4
Observation height above the coil, mm	15
Integration time, s	10
Wavelength, nm:	
As	197.197
B	249.773
P (2d order)	214.911
Si	288.159
W	200.807

PROCEDURES

Samples were diluted with pH 8 NaOH, the amount of dilution depending on the sample type and method. The spectrometer was standardized using a two-point method, a blank and a high standard.

DIRECT METHOD

This method was used to analyze eluates having less than 1 g/L WO_3. Samples were diluted to contain less than 0.1 g/L WO_3 in the aliquot. Feeds, diluted 100-fold, could also be analyzed by this method for arsenic, boron, phosphorus, and silicon. Interelement correction factors were programmed for automatic correction of the interference of tungsten on the other four analytes. Simple aqueous standards were used.

MATCHED STANDARD METHOD

This method was used to determine tungsten in the feed and spent feed samples. The blank and standard contained synthetic brine to approximately match the salt content of the samples, which were diluted 20-fold. Arsenic, boron, phosphorus, and silicon could also be determined simultaneously with tungsten.

INTERNAL STANDARD METHOD

Samples containing 1 g/L or more of WO_3 were analyzed by this method. The spectrometer was standardized with two blanks and a high standard. The pH 8 NaOH served as a blank for tungsten, while a 1.00-g/L-WO_3 solution was used as a blank for arsenic, boron, phosphorus, and silicon. The high standard also contained 1.00 g/L WO_3 and 10 mg/L each of arsenic, boron, phosphorus, and silicon. Tungsten was determined as in the direct method, while the other four analytes were referenced to tungsten, and thus all five elements were determined simultaneously. The samples were diluted to a WO_3 concentration of approximately 1 g/L. No interference corrections were applied.

RESULTS AND DISCUSSION

EFFECT OF MATRIX SALTS

The 450-g/L salt content of the feed brine, spent feeds, and the first one or two eluates affected transfer of the solution into the plasma. These samples required dilution to prevent nebulizer plugging and to lessen the viscosity effect. Test samples were diluted 10, 20, and 100 times. At a dilution of 10, resulting in a salt concentration of 45 g/L, plugging quickly occurred. At a dilution of 20, only occasional plugging occurred, and good results were attainable if the still-high salt content of nearly 23 g/L was matched in the standards. At a dilution of 100, salts presented no problem, and regular standards without matching salt content could be used. Satisfactory results were obtained for arsenic, boron, phosphorus, and silicon on the 100-dilution sample. However, for tungsten concentrations of 80 mg/L or less, results were more variable than desired, and the lower determination limit of about 5 mg/L was inadequate. With a dilution of 20 and matched salt standards, tungsten was determined with good precision to the required 1 mg/L. A series of feed brines containing 80 mg/L WO_3 were analyzed at a dilution of 100 with regular standards and at a dilution of 20 with matching standards. Results are shown in table 3. The matched standard method was also effective at lower tungsten concentrations as found in spent brine. Comparison with colorimetric values is shown in table 4.

TABLE 3. - Tungsten determination in feed brines

	Standard	
	Regular	Matched
Sample dilution.....	100	20
Number of samples.....	11	22
WO_3, mg/L:		
Range.....	72- 90	77-84
Average.....	84	80
Std dev.....	±7	±2
Relative std dev..pct..	7.8	2.4

TABLE 4. - Sample analyses by ICP and other methods, grams per liter

Analyte by sample type and number	ICP	AA[1]	Wet or color
Feed samples:			
WO_3:			
1.....	0.060	ND	0.058
2.....	.081	ND	.079
3.....	.075	ND	.078
As:			
4.....	.19	0.20	ND
5.....	.17	ND	.15
Eluate samples:			
As:			
1.....	<.001	ND	.0002
2.....	.009	ND	.009
3.....	.06	.06	ND
4.....	.22	ND	.22
5.....	1.15	1.1	ND
B_4O_7:			
6.....	.076	<.1	ND
7.....	.33	.33	ND
8.....	.97	1.0	ND
SiO_2:			
9.....	.004	.006	ND
10.....	.056	.06	ND
11.....	.13	.13	ND
12.....	.60	.58	ND
WO_3:			
13.....	.035	ND	.035
14.....	.109	ND	.111
15.....	.586	ND	.595
16.....	1.03	ND	1.01
17.....	5.56	ND	5.51
18.....	13.2	ND	13.5
19.....	47.6	ND	48.8
Spent Feed: WO_3:			
1.....	.0006	ND	<.0007
2.....	.0010	ND	.0009
3.....	.0036	ND	.0036
4.....	.0068	ND	.0065
5.....	.0095	ND	.0092
6.....	.012	ND	.012
7.....	.017	ND	.015
8.....	.022	ND	.022

ND Not determined. [1]Atomic absorption.

Spectral interferences from the matrix salts were limited to slight increases in background which were insignificant at a

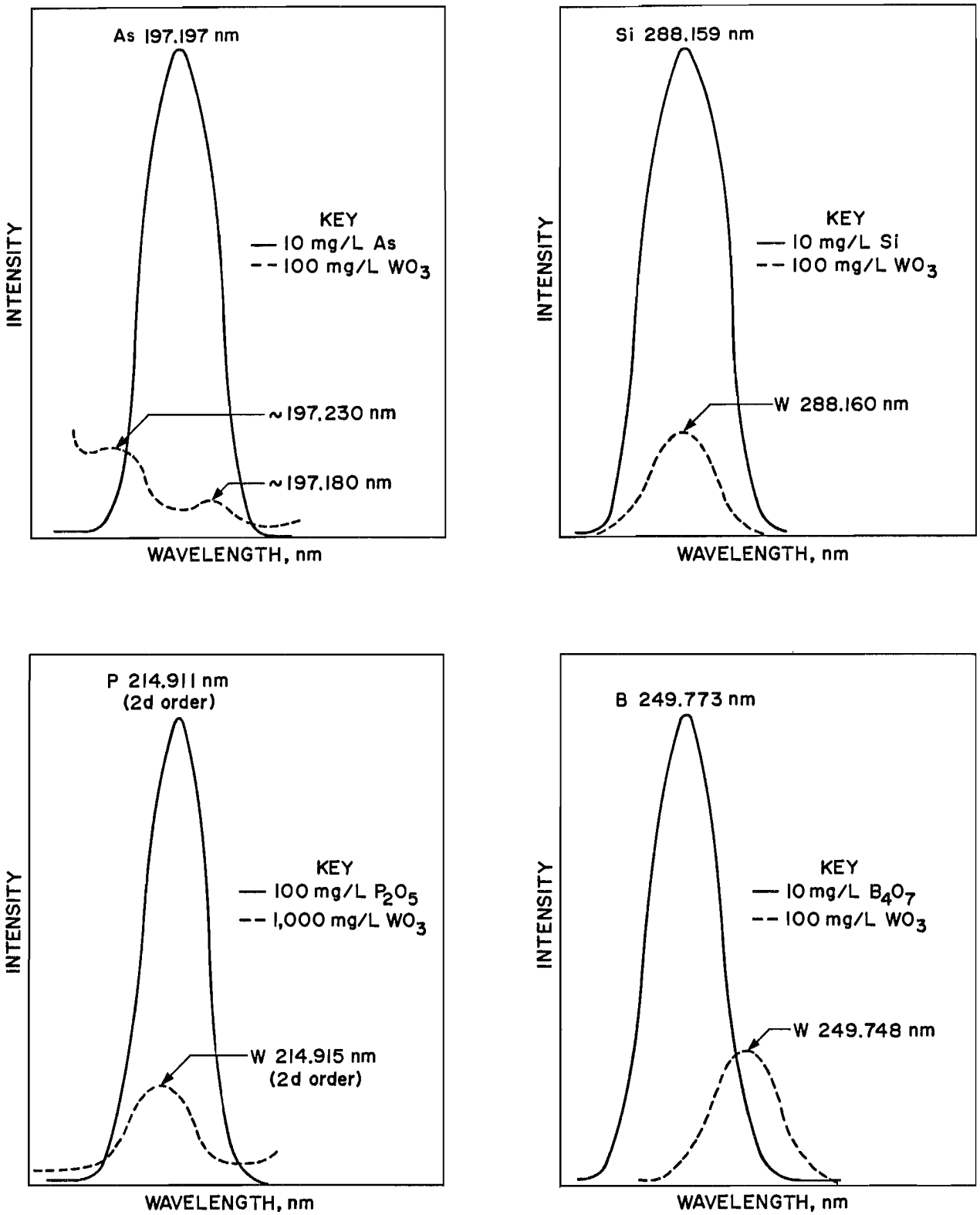

FIGURE 1. - Tungsten interference on arsenic, silicon, phosphorus, and boron.

dilution of 100. Background effect was evident at a dilution of 20, but was eliminated by the matching salt content of the standards.

INTERFERENCES

No significant spectral line interferences were noted from the matrix elements or the analyte elements, with the exception of tungsten. One or more lines of the line-rich tungsten spectrum overlapped the spectral bandpass of each of the other four analytes. Most of the interfering lines are listed in the literature (3-4) and are identified in figure 1, which shows superimposed wavelength profiles for each analyte and tungsten. No listed tungsten lines have as yet been located in the literature for the interferences shown at the arsenic wavelength; D. D. Laun (5) commented in his paper on the W II spectrum that the list of W II lines was not complete but included only classified lines, plus a few stronger unclassified lines.

Three approaches were studied to eliminate the interferences due to tungsten. In the first, or direct method, regular standards were used and interelement interference correction factors were entered into the spectrometer program, which automatically corrected analyte values before printout. Correction factors were determined by burning a solution of pure interfering element--in this case 1 g/L WO_3--and reading out the apparent concentration measured at the analyte wavelength. The factor was then calculated according to the expression

$$F = \frac{\text{apparent analyte concentration}}{\text{interfering element concentration}}$$

and was stored in the computer. During analysis, the factor was multiplied by the measured amount of interfering element present, and the result subtracted from the apparent amount of analyte. This procedure has been described in detail by Marciello (6).

This method was satisfactory when the original samples had tungsten concentrations of less than 1 g/L. At higher tungsten concentrations, variations in the values of the correction factors, a problem also noted by Botto (7-8), significantly raised the lower determination limit. For example, in the case of the large interference of tungsten on phosphorus, the correction factor was sufficiently constant to allow a lower analysis limit of 1 mg/L to be attained if the tungsten concentration did not exceed about 1 g/L. However, assuming a tungsten level of 10 g/L and a not unusual 15-pct variation in the correction factor, the lower analysis limit would be 50 mg/L. Therefore, to apply the direct method to samples with high tungsten levels, it was necessary to determine new correction factors daily and then reprogram the instrument or apply the factors manually. In applying the direct method, samples were diluted to a tungsten concentration of 0.1 g/L or less.

In the second approach, or internal standard method, arsenic, boron, phosphorus, and silicon were referenced to tungsten as the internal standard. The instrument software will accommodate up to four internal standard elements per program. If no element internal standard is used, a low-voltage (-15 V) test channel serves as the internal standard. Tungsten was measured against the test channel and simultaneously served as a variable internal standard for the other analytes. The need for interelement correction factors was eliminated by this technique, and analytes could be determined down to 1 mg/L. The blank and standard each contained 1 g/L WO_3. Samples were diluted to as near this value as was convenient. Tungsten values in the sample aliquot could vary widely and still serve as internal standard, providing good results for the other analytes. The tungsten concentration in the aliquot was maintained between 0.5 and 1.2 g/L WO_3. Analyte values obtained by this approach were comparable to those resulting from the direct method, using current interelement correction factors. Typical results obtained by the two procedures on synthetic samples are given in table 5.

TABLE 5. - Analysis of synthetic solutions by direct and internal standard methods, grams per liter

Solution No. and method[1]	As		B_4O_7		P_2O_5		Si		WO_3	
	Added	Found	Added	Found	Added	Found	Added	Found	Added	Found
1-IS.....	0.040	0.038	0.004	0.004	0	0.001	0	0.001	0.956	0.953
2-IS.....	.004	.004	0	<.001	0	<.001	.040	.042	.956	.955
3-IS.....	0	<.001	.040	.039	.009	.009	0	.001	.956	.961
4-IS.....	.100	.096	0	<.001	0	<.001	.020	.018	1.00	.990
4-D.....	.100	.100	0	<.001	0	<.001	.020	.020	1.00	1.01
5-IS.....	0	<.001	.050	.049	.010	.011	.020	.020	1.00	1.02
5-D.....	0	<.001	.050	.048	.010	.010	.020	.021	1.00	1.04
6-IS.....	.020	.021	.010	.011	.100	.108	0	<.001	1.00	1.04
6-D.....	.020	.021	.010	.009	.100	.096	0	<.001	1.00	1.03

[1]IS = internal standard; D = direct.

In the third approach, tungsten was added to the blank and standard as in the internal standard method, without referencing the other analytes to it. This was effective only when the tungsten concentration in the sample was the same as that in the blank and standard. This was obviously not practical for samples having a wide range of tungsten concentrations.

DETECTION LIMITS, PRECISION, AND ACCURACY

Detection limits, defined here as the concentration equal to two times the standard deviation of the blank, ranged from 0.004 to 0.2 mg/L for the five analytes, as shown in table 6. The one exception was for phosphorus when using the internal standard method. Relative standard deviations were determined on at least ten replicate burns. The results are shown in table 7. Except for phosphorus in almost all samples, silicon in high eluates, and tungsten at 1 mg/L in a spent feed, relative standard deviations were 2 pct or less.

Accuracy was evaluated using synthetic samples and by comparison with non-ICP methods. Synthetic samples, containing approximately 1 g/L WO_3, were analyzed by the direct and internal standard methods. The results of these analyses are given in table 5. Arsenic, boron, silicon, and tungsten values in feeds, eluates, and spent feeds obtained by the applicable ICP procedure are compared with colorimetric, wet chemical, and atomic absorption values in table 4. The average deviation for all compared values was about 2.5 pct.

TABLE 6. - Analyte detection limits, milligrams per liter

Procedure and blank	As	B_4O_7	P_2O_5	Si	WO_3
Direct: NaOH, pH 8.....	0.024	0.007	0.20	0.004	0.05
Matching standard: 1/20 synthetic brine	.052	.010	.17	.040	.11
Internal standard:					
1.0 g/L WO_3.....	.062	.048	.43	.082	NAp
NaOH, pH 8.....	NAp	NAp	NAp	NAp	.20

NAp Not applicable.

TABLE 7. - Precision: Average of 10 determinations and percent relative standard deviation (RSD)

Procedure	As		B_4O_7		P_2O_5		Si		WO_3	
	Av g/L	RSD, pct	Av g/L	RSD, pct	Av g/L	RSD, Pct	Av g/L	RSD, pct	Av g/L	RSD, pct
Direct:										
Feed brine.....	0.193	1.37	9.14	0.60	0.630	4.47	0.011	2.08	NAp	NAp
Low eluate 1.....	.010	1.33	1.53	.61	.015	3.62	.025	.47	0.082	0.70
Low eluate 2.....	.017	1.97	.167	.51	.008	9.80	.004	1.37	.545	.24
Low eluate 3.....	.033	1.25	1.51	.87	.029	5.18	.021	1.47	1.12	.52
Matching standard:										
Feed brine.....	.190	.87	8.95	.97	.600	1.53	.010	.94	.079	1.82
Spent brine 1.....	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	.005	1.51
Spent brine 2.....	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	.001	7.4
Internal standard:										
High eluate 1.....	.057	1.25	.029	2.02	.081	4.56	.017	5.44	3.79	.93
High eluate 2.....	.181	1.00	.139	1.51	.218	4.79	.055	5.33	10.9	.97
High eluate 3.....	1.57	1.40	.203	1.84	1.76	5.32	.041	11.4	81.2	1.11

NAp Not applicable.

CONCLUSION

Inductively coupled plasma spectrometry was an effective method for the rapid, accurate determination of tungsten, arsenic, boron, phosphorus, and silicon in Searles Lake brine and related process solutions. The effects of high salt content were eliminated by sample dilution and using standards of matching salt content. Tungsten interferences on the other four analytes were corrected by programmed interelement interference corrections for concentrations of tungsten up to 1 g/L. For tungsten concentrations of 1 to 100 g/L, the interference was corrected by using a standard and blank containing 1 g/L WO_3, and referencing the other four analytes to tungsten. The average precision for all analytes was 2.5 pct relative standard deviation.

REFERENCES

1. Altringer, P. B., W. N. Marchant, R. O. Dannenberg, and P. T. Brooks. Tungsten Recovery From Searles Lake Brines. BuMines RI 8315, 1978, 15 pp.

2. Altringer, P. B., P. T. Brooks, and W. A. McKinney. Selective Extraction of Tungsten From Searles Lake Brines. Pres. at BuMines Symp. on Separation Science and Technology for Energy Applications, Gatlinburg, TN, May 5-8, 1981; available upon request from Jean B. Beckstead, Librarian, Salt Lake City, UT.

3. Harrison, G. R. (ed.). Massachusetts Institute of Technology Wavelength Tables. MIT Press, Cambridge, MA, rev. ed., 1969, 429 pp.

4. Laun, D. D., and C. H. Corliss. The First Spectrum of Tungsten (W I). J. Res. NBS, v. 72A, 1968, pp. 609-755.

5. _____. Second Spectrum of Tungsten (W II). J. Res. NBS, 68A, 1964, pp. 207-252.

6. Marciello, L., and A. F. Ward. Technical Aid Note #3: Interelement Corrections for Spectral Line Interferences. Jarrell-Ash Plasma Newsletter, v. 1, No. 1, Jan. 1978, pp. 12-13.

7. Botto, R. I. Interference Calibration and Correction Procedure for ICPES Direct Reading Spectrometers. ICP Inf. Newsletter, v. 7, No. 2, July 1981, pp. 74-75.

8. _____. Long Term Stability of Spectral Interference Calibrations for Inductively Coupled Plasma Atomic Emission Spectrometry. Anal. Chem., v. 54, 1982, pp. 1654-1659.

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